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# Short-range spin-phonon coupling in in-plane CuO nanowires: a low-temperature Raman investigation

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## Abstract

We report an application of low-temperature Raman scattering on in-plane CuO nanowires, in which an overview of the characteristic parameter of spin-phonon coefficient, the interaction of incident light with the spin degrees of freedom, and size effects will be given. The appearance of spin-phonon coefficient decrease reflects the existence of finite size effect.

**Keywords:** Raman spectroscopy; Cupric oxide; Nanowire; Spin-phonon coupling

## Background

Low-dimensional nanosized effects in CuO systems, especially their different physical properties such as spin-spin [1,2], electron-phonon [3], spin-phonon interactions [4], and giant negative thermal expansion have recently received a lot of attention [5]. The spin-spin superexchange interaction occurs via the oxygen orbital [4,6]. The magnetic interactions and Néel transition temperature ( $T_N$ ) of the CuO system are strongly dependent on the exchange interaction and the number of neighboring atoms. A transition from a first-order transition to a commensurate antiferromagnetic state near  $T_N \sim 213$  K reported for bulk CuO from neutron scattering experiments [7,8] is well understood. Controlling the size of CuO nanocrystals resulted in short-range correlation and commensurate antiferromagnetic (AFM) ordering, where the  $T_N$  decreased from the bulk value of 213 K [9–11], with decreasing particle size, down to 40 K for 6.6-nm nanoparticles [1,2] and 13 K for 2- to 3-nm nanorods [12]. It is known that spin-phonon coupling is usually weak and undetectable because symmetric vibrations of relevant atoms will cancel the contributions from negative and positive displacements. The main feature of cupric oxide is the low-symmetry monoclinic lattice, which differs from the other transition metal monoxides, e.g., MnO, FeO, CoO, and NiO with rock salt structure [13]. The low symmetry of the CuO lattice

and the anisotropic dispersion curves indicated lattice vibration which caused a modulation of the spin-phonon interaction. This originated from slight changes in the inter-ionic distances and bond angles, leading to spin-phonon coupling that can be detected in the Raman spectrum, to produce a weak feature at about  $230\text{ cm}^{-1}$  below  $T_N$  [14,15]. The discovery of spin-phonon coupling in CuO nanocrystals has led to renewed interest in this phenomenon. Up to now, there have been few experimental alternatives for the determination of the size effect of spin-phonon coupling of CuO nanowires. In this study, low-temperature Raman spectroscopy is employed to investigate the size effects of spin-phonon coupling in in-plane CuO nanowires. Low-temperature Raman spectroscopy has the high spatial resolution and sensitivity necessary for probing the local atomic vibrations of nanowires. Our results reveal that below Néel temperature there is a ready shift of the spin-phonon coefficient  $\lambda_{sp}$  decreases as the mean diameter of in-plane CuO nanowire decreases, exhibiting a long- to short-range spin-phonon coupling that can be nicely described with the expected theoretical order parameter as due to antiferromagnetic ordering in in-plane CuO nanowires.

## Methods

A series of in-plane CuO nanowires with various diameters were fabricated. The samples were prepared by a process where a pure copper grid was placed in a ceramic boat inside a quartz tube, which was then

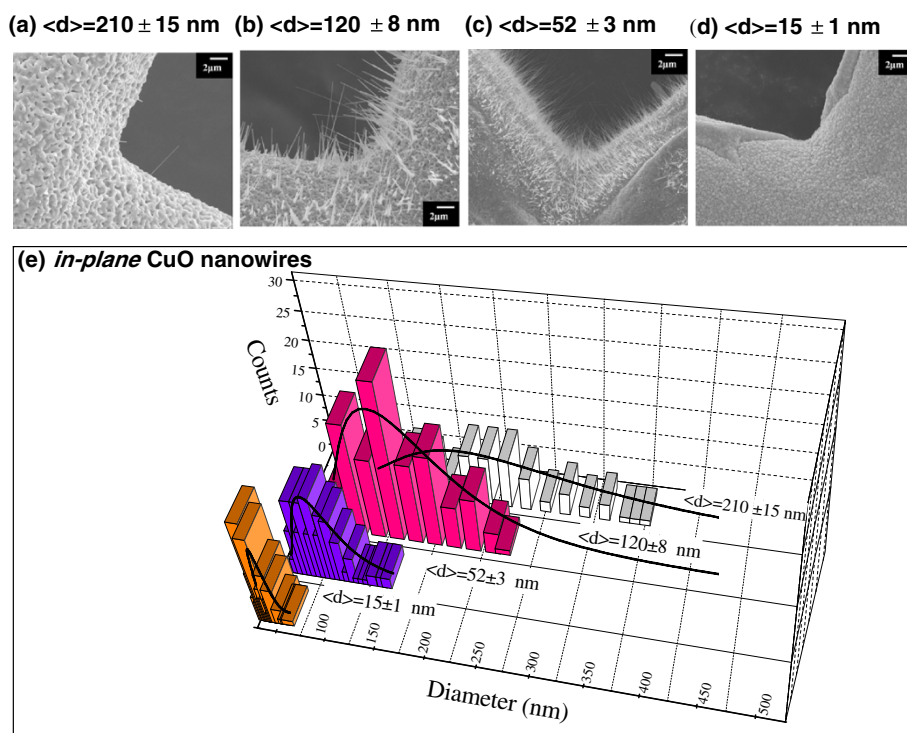
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evacuated to about  $10^{-3}$  Torr using a mechanical pump. They were then heated in a tube furnace at about  $200^{\circ}\text{C}$  for 2 h for degassing, after which the samples were heated to various temperatures ranging from  $300^{\circ}\text{C}$  to  $600^{\circ}\text{C}$  for 2 h under mixed argon (100 sccm) and oxygen (10 sccm) gas. Details of specimen preparation and characterization have been described in a previous paper [16]. Transmission electron microscopy (TEM) and high-resolution transmission microscopy (HRTEM) images from a JEM-3010 transmission electron microscope (JEOL Ltd., Tokyo, Japan) were obtained to study the crystalline structure. The results of an early study show that the prepared nanowires are crystalline [16], revealing a monoclinic unique Y structure with lattice parameters of  $a = 4.63 \text{ \AA}$ ,  $b = 3.55 \text{ \AA}$ ,  $c = 5.16 \text{ \AA}$ , and  $\beta = 99^{\circ}52'$ . The morphology of the prepared nanowires was characterized using field-emission scanning electron microscopy (FESEM; JEOL JSM-6500 F). The SEM images in Figure 1a,b,c,d show the morphology of the CuO nanowires with various diameters which were synthesized at  $T = 600^{\circ}\text{C}$ ,  $500^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$ , and  $300^{\circ}\text{C}$ , respectively. It can be seen that the in-plane CuO grew homogeneously on the copper grid substrate to form straight nanowires. Observation of uniform nanowires (with lateral dimensions in the nanoscale order of tens to hundreds nanometers) shows that they grew up to a few microns in length. Figure 1e shows that the

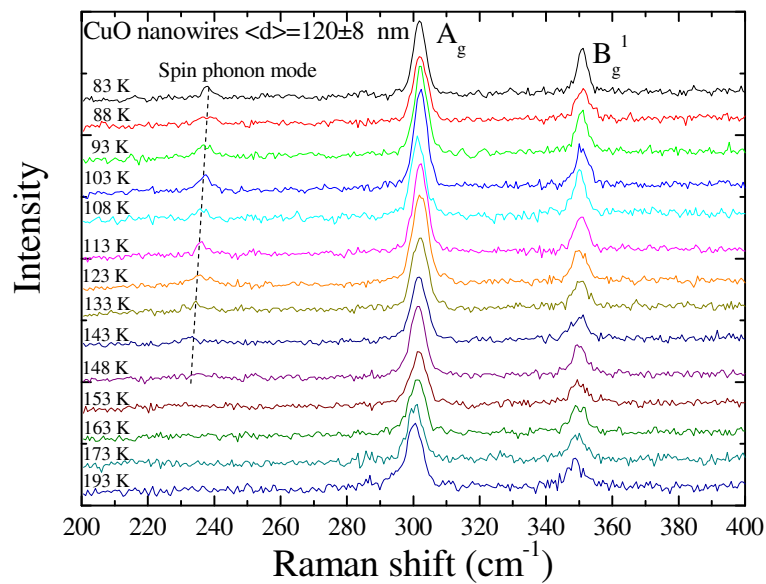
distribution of the nanowires was quite asymmetric. The solid lines represent the fitting curves assuming the log-normal function<sup>a</sup>. The mean diameters obtained from the fits of log-normal distribution are  $\langle d \rangle = 210 \pm 15 \text{ nm}$ ,  $120 \pm 8 \text{ nm}$ ,  $52 \pm 3 \text{ nm}$ , and  $15 \pm 1 \text{ nm}$ , respectively. The value obtained for the standard deviation of the distribution profile  $\sigma$  reveals that the increase with broadening was presumably due to the crystalline effects.

## Results and discussion

All low-temperature Raman spectra were measured using a Jobin Yvon 64000 Raman microscope (HORIBA, Minami-ku, Kyoto, Japan) equipped with a Linkam optical DSC system (THMS600; Linkam Scientific Instruments, Surrey, UK). The results were utilized to investigate the spectroscopic properties of CuO nanowire at various temperatures. The specimens were mounted on a non-background sample holder fixed to a cold head in a high-vacuum ( $<10^{-3}$  Torr), low-temperature (approximately 80 K) chamber. The CuO nanowire was excited by focusing a 514.5-nm Ar ion laser (Coherent Inc., Santa Clara, CA, USA) with a 5-mW laser power on the sample to form a spot size of approximately  $1 \mu\text{m}$  in diameter, giving a power density of  $10^2 \text{ W/cm}^2$ . From the factor group analysis of the zone center modes for the monoclinic structure, given by Rousseau et al. [17], there are three



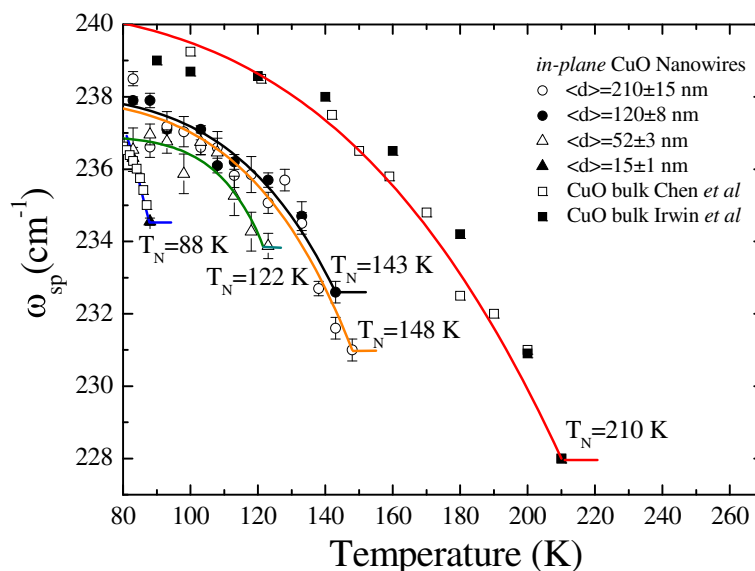
**Figure 1 Morphology of the in-plane CuO nanowires.** SEM images of the in-plane CuO nanowires synthesized at various temperatures (a, b, c, d). The distributions of the mean diameter of the nanowires obtained from a portion of the SEM image (e). The solid lines represent the fitting curves assuming the log-normal function, where  $\langle d \rangle$  is the mean diameter of the nanowires.



**Figure 2** Series of Raman spectra taken at various temperatures of CuO nanowires with a mean average diameter  $\langle d \rangle = 120 \pm 8$  nm. Two main phonon modes corresponding to the  $A_g$  and  $B_g^1$  symmetries, respectively, are revealed. As the temperature was reduced to 143 K, a well-defined peak at  $238 \text{ cm}^{-1}$  developed, signifying the spin-phonon coupling.

Raman active modes ( $A_g$ ,  $B_g^1$ , and  $B_g^2$ ) predicted in the spectra of CuO nanowires. Figure 2 shows an example of a series of Raman spectra taken at various temperatures, covering the antiferromagnetic transition temperature, with a mean diameter of  $120 \pm 8$  nm. There are two phonon modes revealed in the Raman spectra taken of the CuO nanowires at  $T = 193 \text{ K}$  at  $300.2$  and  $348.8 \text{ cm}^{-1}$  [18], which are related to  $A_g$  and  $B_g^1$  symmetries [19,20]. The peak position is lower than the value of the bulk CuO

( $A_g = 301 \text{ cm}^{-1}$  and  $B_g^1 = 348 \text{ cm}^{-1}$ ) [21], reflecting the size effect which acts to confine the lattice vibration in the radial directions resulting in a shift in the  $A_g$  and  $B_g^1$  symmetries. As the temperature decreases to 83 K, it can be clearly seen that the peak positions of the  $A_g$  and  $B_g^1$  modes around  $301.8$  and  $350.9 \text{ cm}^{-1}$ , shown at the top of Figure 2, shifted toward higher Raman frequencies. While the temperature increased from 83 to 193 K, the peak position of the  $A_g$  mode softened by 0.7%. Since the frequency



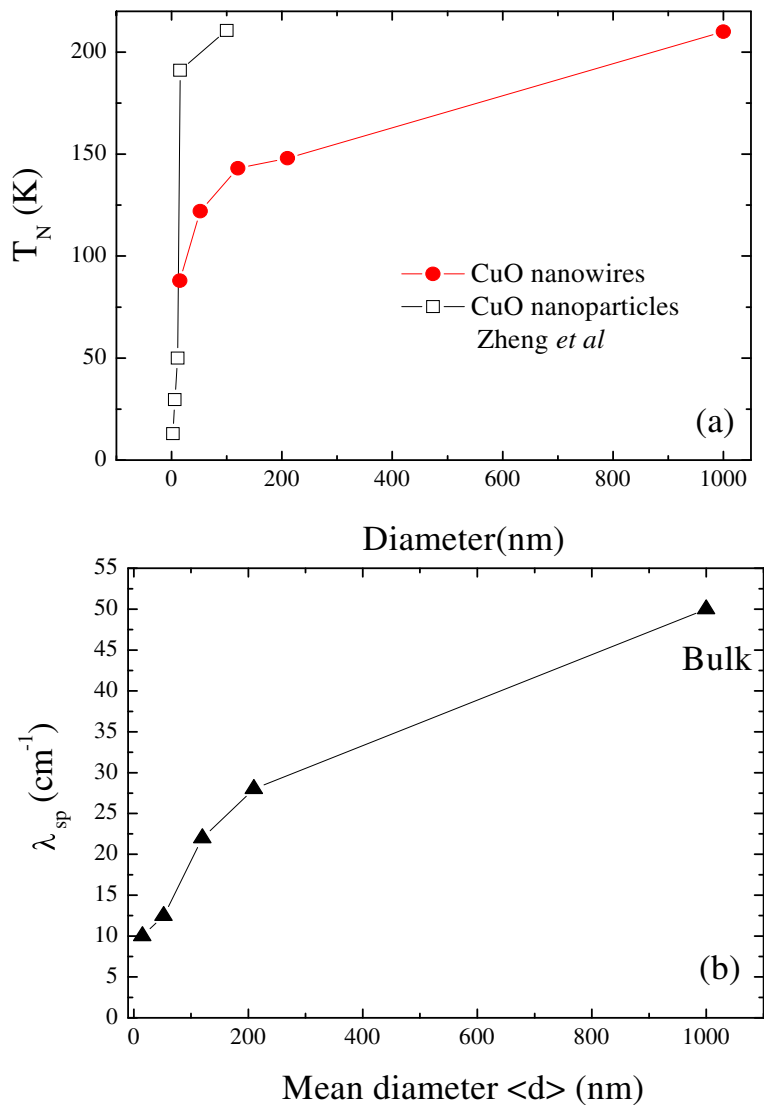
**Figure 3** Temperature variations of the spin-phonon modes of CuO nanowires with various mean diameters. The solid line represents the fit by the ordering parameter.

**Table 1 Summary of the fitting results of the in-plane CuO nanowires**

Size (nm)	$T_N$ (K)	$\omega_{sp}^o$ ( $\text{cm}^{-1}$ )	$\lambda_{sp}$ ( $\text{cm}^{-1}$ )	$\gamma$
Bulk <sup>a</sup>	210	228	50	$3.4 \pm 0.2$
$210 \pm 15$	148	231	28	$4.5 \pm 0.5$
$120 \pm 8$	143	232.6	22	$5.1 \pm 0.2$
$52 \pm 3$	122	233.8	12.48	$8 \pm 1$
$15 \pm 1$	88	234.5	10	$20 \pm 5$

<sup>a</sup>From [8,15].

of the phonon mode is related to Cu-O stretching, it is expected that the frequency will downshift with increasing temperature, primarily due to the softening of the force constants that originate from the thermal expansion of the Cu-O bonds, resulting from the change in vibrational amplitude [22,23]. In the study, the high resolution of our spectrometer allowed detection of relative change as small as  $0.5 \text{ cm}^{-1}$ , and the vibrational frequency of a phonon mode can be used to determine the spin-phonon interaction. A phonon-phonon effect originates from the dynamical motion of lattice displacements, which are strongly coupled to the spin degrees of freedom dynamically below the magnetic ordering temperature. This coupling between the lattice and the spin degrees of freedom is named as spin-phonon. As shown in Figure 2, with



**Figure 4 Size effects of Néel temperature and spin-phonon coupling coefficients.** The obtained Néel temperature (a) and spin-phonon coupling coefficients (b) as a function of mean diameter, which showed a tendency to decrease with reduction in diameter.

decreasing temperature, a well-defined peak developed at  $231\text{ cm}^{-1}$  signifying the spin-phonon coupling [8,19] which shows that a noticeable shift to lower frequency is sensitive to the temperature variation.

Figure 3 shows the temperature dependence of the spin-phonon mode for in-plane CuO nanowires of various diameters. Typical examples for bulk CuO are shown in Figure 3, indicated by open and solid squares [8]. It has been suggested in previous reports that the temperature dependence of the spin-phonon mode (the origin of the peak at  $228\text{ cm}^{-1}$ ) might be associated with magnetic ordering, the frequency shift corresponding to the spin-correlation function times a spin-phonon coupling coefficient  $\lambda_{\text{sp}}$ . The temperature dependence of the spin-phonon peak can be represented as  $\omega_{\text{sp}} = \omega_{\text{sp}}^0 + \frac{1}{4} \lambda_{\text{sp}} \phi(T)$ , where  $\omega_{\text{sp}}^0$  is the Raman shift in the absence of spin-phonon coupling at  $T_N$  and  $\phi(T)$  is the order parameter estimated from the mean field theory [24]. The order parameter can be described as  $\phi(T) = 1 - (T/T_N)^\gamma$ , where the order parameter  $\gamma$  varied from  $3.4 \pm 0.2$  to  $20 \pm 5$ . The solid curves indicate the theoretical fitting, and the corresponding parameters are presented in Table 1. The size effect acts to confine the spin-phonon coupling by increasing the  $T_N$  from 210 to 88 K, as shown in Figure 4a, when the size is reduced from bulk to  $15 \pm 1\text{ nm}$  (see for comparison  $T_N = 213\text{ K}$  for CuO single crystal and powder [8,16]). The obtained spin-phonon coupling coefficient  $\lambda_{\text{sp}}$  also tends to decrease with decreased phonon amplitudes as the diameter decreased, as shown in Figure 4b, revealing the existence of short-range coupling. This result is consistent with past reports which state that the magnetic transition temperature of  $\text{Cr}_2\text{O}_3$  [25,26] and CuO nanoparticles (open square) is reduced [12], which can be attributed to the fact that the ground state fails to develop long-range antiferromagnetic ordering. This occurs because of quantum lattice fluctuations and being energetically favorable to some kinds of short-range order state, resulting in a lower spin-phonon coefficient with reduced size [27,28]. The magnitudes of these obtained  $\lambda_{\text{sp}}$  values are intermediate compared to approximately  $1\text{ cm}^{-1}$  for  $\text{FeF}_2$  and  $\text{MnF}_2$  [24], and approximately  $50\text{ cm}^{-1}$  for bulk CuO [8], indicating that the size effects could result in a tendency to weaken the strong spin-phonon coupling. A minimum spin-phonon coefficient of  $\lambda_{\text{sp}} = 10\text{ cm}^{-1}$  was obtained in  $\langle d \rangle = 15 \pm 1\text{ nm}$  in-plane CuO nanowires, which was found to be weaker by a factor of 0.018 than the nearest neighbor spin-spin coupling strength of  $J = 552\text{ cm}^{-1}$  for one-dimensional antiferromagnetic Heisenberg chain [29]. In general, the spin-orbit interaction will induce a small orbital moment, which couples the magnetic moment to crystalline axes of the phonon vibration. Anharmonic effects are expected and caused the phonon and spin contribution to mix because the  $\lambda_{\text{sp}}$  decreases as the diameter of the CuO nanowires decreases.

## Conclusions

In conclusion, we investigate the size dependence of CuO nanowires and the nanosized spin-phonon effects. Raising the temperature and decreasing the diameter of CuO nanowires result in the weakening of spin-phonon coupling. The temperature variations of the spin-phonon mode at various diameters are in good agreement with the theoretical results. We found that the spin-phonon mode varies with the size of the CuO nanowires and in corroboration with the strength of spin-phonon coupling. Our result reveals that low-temperature Raman scattering techniques are a useful tool to probe the short-range spin-phonon coupling and exchange energy between antiferromagnetic next-nearest neighboring magnons in nanocrystals below the Néel temperature. The application of low-temperature Raman spectroscopy on magnetic nanostructures represents an extremely active and exciting field for the benefit of science and technology at the nanoscale. The rising new phenomena and technical possibilities open new avenues in the characterization of short-range spin-phonon interactions but also for the understanding of the fundamental process of magnetic correlation growth in nanomaterials.

## Endnote

<sup>a</sup> The log-normal distribution is defined as follows:

$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln d - \ln \langle d \rangle)^2}{2\sigma^2}\right)$ , where  $\langle d \rangle$  is the mean value and  $\sigma$  is the standard deviation of the function.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

SYW wrote, conceived of, and designed the experiments. PHS grew the samples and analyzed the data. CLC contributed the Raman experimental facility and valuable discussions. All authors discussed the results, contributed to the manuscript text, commented on the manuscript, and approved its final version.

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